

Vibrational Spectra of Estane® 5703

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Estane® 5703 is a polymeric elastomer that is used as part of the binder in the high-explosive (HE) formulation PBX 9501. How this polymer chemically degrades as it ages, and how that is then reflected in its mechanical properties and the properties of PBX 9501 are important issues for the surety of the stockpile. Other Estane® materials (and closely related formulations) are used in a wide variety of commercial applications as well, and similar questions about their aging and changes in mechanical properties are also quite significant issues. This project, which is studying the vibrational spectra of Estane® and how it responds to different thermal and mechanical perturbations, is part of a larger program that is developing a physically-based model of the material, including its aging characteristics.

Estane® materials are segmented block copolymers of polyester and polyurethane, and they undergo a microphase separation where the urethane moieties attempt to self-aggregate. This process is thermally reversible, with the majority of the separation occurring over several hours at room temperature, though changes continue to occur over month-long time periods. A signature of the urethane aggregation is the hydrogen bonding that occurs between the urethane (carbamate) units, which gives rise to changes in the vibrational spectra of the material. This project is analyzing and modeling those spectral shifts in order to develop an atomistic picture of the macroscopic response of the material.

Figure 1 shows the experimental infrared (IR) spectra of Estane® 5703 at two different times after casting, where the sample has been heated to 110°C which melts it and disrupts any microphase separation. The first spectra (black) is taken within 15 minutes after cooling the sample back down to room temperature,

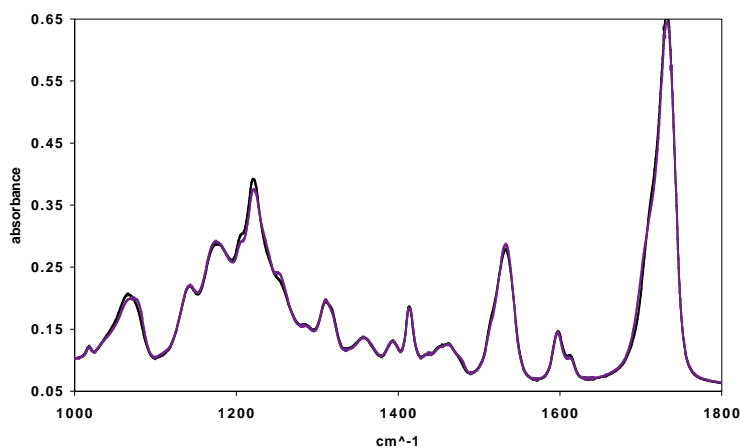


Figure 1.

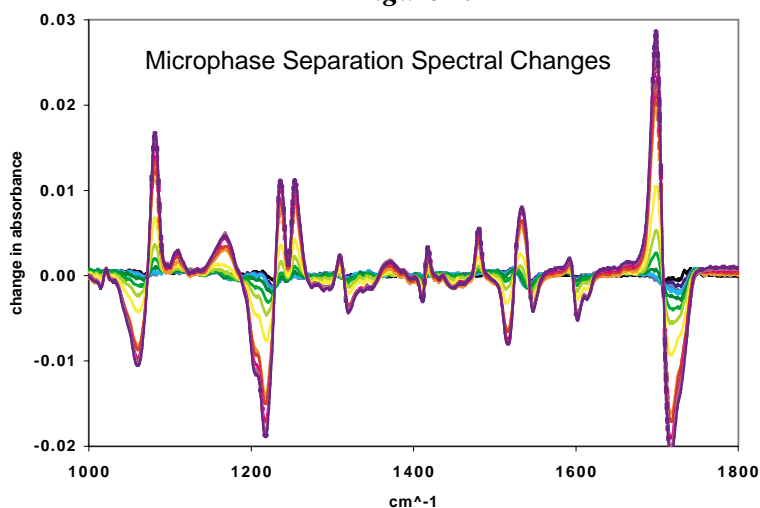


Figure 2.

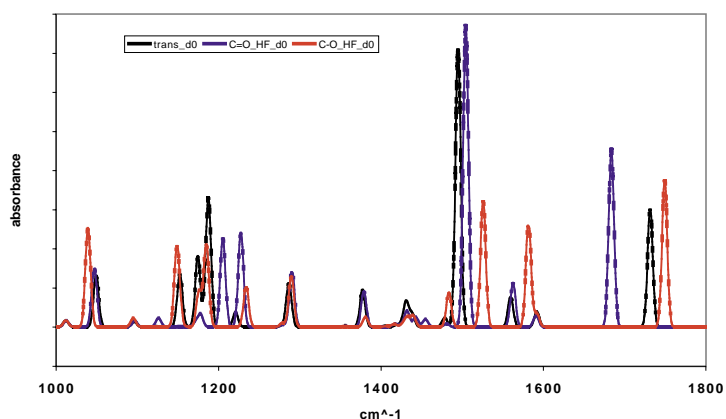


Figure 3.

which is also before any significant solidification has occurred. The second spectrum (purple) is from the same sample one week later. Changes in the IR spectra are apparent though subtle on this scale. Shown in Figure 2 are the difference spectra at various times relative to the initial spectra at 15 minutes. The times when these spectra were collected are distributed logarithmically between 15 minutes and one week and are color coded by a rainbow scheme of blue to purple. This highlights the spectral changes more dramatically and shows them to be consistent and quantifiable. This also shows that the separation process follows a two-step process: there is one set of slight spectral changes at early times (< 2 hours blue to dark green), followed by a much stronger set of changes at later times (green to purple). This two-step kinetic process is also observed in the substantial changes in the shear modulus of the material for the same thermal treatment.

Figure 3 shows some examples of calculated spectra for a model urethane compound (methylphenylcarbamate) and what spectral changes occur for different types of hydrogen bonding (using HF as a hydrogen donor). These were ab initio calculations using the Gaussian98 method with a DFT B3LYP 6-31G** basis set. The black spectra is that

calculated for the starting material, the blue is that for HF hydrogen-bonding to the carbonyl oxygen, and the red is for the HF hydrogen-bonding to the ether-type oxygen. It is found that rather extensive spectral changes accompany these seemingly minor interactions, and that these match many of the observed spectral changes. In combination with numerous other calculations, these results show that most of the spectral changes are associated with the polyurethane half of the polymer (though some changes in the polyester spectra are also observed), and that the microphase separation process is accompanied by hydrogen-bond formation and by the transference of hydrogen-bonds from ether to carbonyl oxygen atoms.

Similar complex spectral shifts as well as polarization changes are observed when these samples are stretched. Analysis of those systems reveals which parts of the polymer reorient with the deformation and how the imposed stress is supported on an atomistic basis. Isotopic labeling is also being used and analyzed to fully characterize the spectroscopic band assignments and effective force fields for these molecules. These are being interpreted and quantified with the aid of these quantum chemical calculations.

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